Final Report for Period: 08/2010 - 01/2011
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Award ID: 0643139
Principal Investigator: Stack, Andrew G.
Organization: GA Tech Res Corp - GIT
Submitted By:
Stack, Andrew - Principal Investigator
Title:
Testing Molecular Mechanisms for Growth and Dissolution Reactions on Calcite Surfaces

Project Participants

Senior Personnel

Name: Stack, Andrew
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Graduate Student

Undergraduate Student

Technician, Programmer

Name: Grantham, Meg
Worked for more than 160 Hours: Yes
Contribution to Project:
Ms. Grantham is collecting data for the project since a graduate student has not yet been found.

Other Participant

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

None.

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)
Research Activities:

In performing the work funded by NSF proposal EAR 0643139 entitled, ?Testing Molecular Mechanisms for Growth and Dissolution Reactions on Calcite Surfaces?, we have worked on a variety of subjects, ranging from the state goals of the project to measure calcite growth and dissolution with the aim of determining the molecular mechanisms for growth, as well as investigated the dissolution of iron (oxy)(hydr)oxides in the presence of iron reducing bacteria.

In years one and two, we measured growth rate of monomolecular calcite steps in situ using the atomic force microscope under a fixed saturation state but varying aqueous calcium-to-carbonate ratio and derived a new crystal growth theory to explain the results. In year three, we have measured growth of calcite steps as a function of aqueous calcium-to-carbonate ratio in the presence of the growth inhibitor strontium as well as under variable saturation state. For the variable saturation state experiments, we measured the growth of calcium carbonate under varying aqueous calcium-to-carbonate ratio but constant saturation index (SI = log [aCa⋅aCO3/Ksp]). We did this for two different SI values, and applied the crystal growth model derived in year two to both.

For the strontium experiments, we initially reproduced previous measurements in this system by Dove and coworkers (Wasylenki et al., 2005, Geochim. Cosmochim. Acta, 69, 3017-3027) and found good agreement. In order to select conditions where there was a readily observable effect of strontium, but growth was not poisoned entirely, we then measured step velocity as a function of strontium concentration but with saturation state fixed. Having selected a suitable strontium concentration, we measured step velocity as a function of aqueous calcium-to-carbonate ratio and fit the results to the crystal growth theory derived in year two.

We are still in the process of confirming these data and will publish the results soon thereafter. Two additional manuscripts from work in years 1 & 2 of this project were published in January of this year (see publications section of report).

For the experiments on the dissolution of iron (oxy)(hydr)oxides in the presence of iron reducing bacteria, we first investigated the dissolution morphologies of these minerals under a variety of conditions using the atomic force microscope. Control experiments were performed, followed by exposure to wild-type Shewanella oneidensis MR-1, then mutants of this species unable to respire on iron minerals without the aid of an exogenous electron shuttle, as well as abiotic controls without bacteria. We found the the wild-type organisms produce dissolution morphologies that are difficult to explain using a small, soluble electron shuttle. It supports the notion that the wild type organism does not use an endogenous electron shuttle of this type.

Secondly, we observed that clustering of the organisms on the surface was occurring. We measured the attachment of bacterial cells in situ using a confocal microscope and a live-dead dye. We found that the adsorption isotherm for the bacterial cells did not follow the standard isotherm forms (Langmuir, Freundlich) for abiotic adsorbates because of the formation of microcolonies of organisms.

Educational Activities:

This research is having some broader impacts beyond its intellectual merit. Firstly, the project formed the bulk of the support for a Ph.D. student, Mengni Zhang, who successfully defended her dissertation in August, 2010 and is now working at an environmental consulting firm based in Atlanta, Georgia. She is now applying her knowledge of biogeochemistry to directly address field-scale environmental problems. Second, the project funded the PI and three of his students to report their results at three annual Goldschmidt Geochemical Society meetings in Knoxville Tennessee, Cologne Germany, and Davos Switzerland. In addition to Dr. Zhang, the two students were Ms. Jacquelyn Bracco and Mr. Davis Warren. Ms. Bracco was an undergraduate who has now decided to undertake a Masters of Science degree with me based in part on her experiences on this project, while Mr. Warren is a Masters of Science student in his first year. This project also gave partial support to an undergraduate, Ms. Cyndi Jackson, who performed some experiments for me under Dr. Zhang?s project.

Additionally, results from this work were used in the PI?s graduate level Mineral Surface

Geochemistry course.

Findings: (See PDF version submitted by PI at the end of the report)

Over the course of this project, we have made significant advances in establishing the validity of the crystal growth model derived in years 1 and 2. Firstly, in experiments where the saturation index was kept constant but the ratio of aqueous calcium-to-carbonate ratio was varied, we found that the model gave similar rate constants for attachment and detachment under two different saturation states. This confirms that the variables in the model that were initially assumed to be constant are in fact, constant. The implication of this result is that the previously derived model can predict growth as a function of saturation state and aqueous calcium-to-carbonate ratio, something we had not established in years 1 and 2 of this project since we had always worked under the same saturation index. Existing kinetic models do not account for variation in the constituent mineral?s aqueous cation-to-anion ratio. Since this parameter is known to strongly affect growth rate, this represents a significant advance in moving towards a molecular-level mineral growth and dissolution model.

In the second half of this year, we measured the growth of calcite under fixed saturation state but varying aqueous calcium-to-carbonate ratio in the presence of the growth inhibitor strontium. Our results showed that strontium preferentially impedes crystal growth under conditions where carbonate is limiting, i.e. high Ca/CO3 ratios. The model fit to this data using our previously established theory gives similar rate constants for attachment and detachment of calcium, but significantly impeded rate constants for attachment and detachment of carbonate. This strongly suggests that strontium impedes crystal growth by labilizing carbonate ion on the calcite surface. While this result was hypothesized by the PI and othesr, it has not been demonstrated before, and again in that most crystal growth studies in this system keep the the ratio of calcium-to-carbonate constant. Thus, this result also represents a significant improvement in our understanding of mineral growth at the molecular-level.

Additionally, the project helped us to determine that a common iron reducing organism, Shewanella oneidensis strain MR-1, produced dissolution morphologies that are not easily explainable using a small, soluble electron shuttle. This result will help us understand the mechanism of iron reduction by dissimilatory iron reducing bacteria. We followed this finding up with a measurement of attachment of this organism to iron (oxy)(hydr)oxide mineral coatings. We derived a isotherm that accounted for the ability of this organism to create microcolonies above a critical cell density. Combined, this work will be helpful in predicting the bioavailability of iron (oxy)(hydr)oxide minerals in the subsurface.

Training and Development:

This work supported one Ph.D. student, Ms. Mengni Zhang, who completed her degree in fall, 2010. She is currently working at a position at an environmental consulting firm dealing with bioremediation of pollutants. She received this position as a direct result of her activities supported by this project.

Secondly, this project partially supported the research projects of two undergraduate students, Ms. Jacquelyn Bracco and Ms. Cyndi Jackson. They received training in atomic force microscopy and kinetic studies (Bracco) and in sample preparation, microbiology and confocal microscopy (Jackson). Ms. Bracco presented her results at the 2010 Annual Goldschmidt Geochemistry Society conference in Knoxville, TN. Ms. Bracco decided to do a Master's of Science under the PI starting fall 2010, a decision based in part by her support under this project.

Lastly, this work supported the training of one first year Master's of Science student, Mr. Davis Warren, on molecular dynamics and rare event theories.

Outreach Activities:

Results from this project were presented at the 2007, 2008 and 2010 Annual Goldschmidt Geochemical Society conferences. Also, the work was included in the courses of the PI, especially his Mineral Surface Geochemistry course. Lastly, this project helped support a K-12 school teacher, Ms. Kari Salomon, from a local middle school. Ms. Salomon spent the summers of 2007 and 2008 in my laboratory doing an internship and learning about biogeochemistry. The PI also gave a lecture on minerals and atoms to her 8th grade Earth Science students. Ms. Salomon directly included what she learned during her internship into her coursework in the form of new exercises, laboratory experiments, and learning material for her 8th grade Earth Science course.

Journal Publications

Zhang, MN; Dale, JR; DiChristina, TJ; Stack, AG, "Dissolution Morphology of Iron (Oxy)(Hydr)Oxides Exposed to the Dissimilatory Iron-Reducing Bacterium Shewanella oneidensis MR-1", GEOMICROBIOLOGY JOURNAL, p. 83, vol. 26, (2009). Published, 10.1080/0149045080266056

Zhang M; Ginn BR; DiChristina TJ; Stack AG, "Adhesion of Shewanella oneidensis MR-1 to iron (oxy)(hydr)oxides: Microcolony formation and isotherm", Environmental Science and Technology, p. 4602, vol. 44, (2010). Published, 10.1021/es901793a

Stack AG; Grantham MC, "Growth Rate of Calcite Steps As a Function of Aqueous Calcium-to-Carbonate Ratio: Independent Attachment and Detachment of Calcium and Carbonate Ions", Crystal Growth and Design, p. 1409, vol. 10, (2010). Published, 10.1021/cg901395z

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

We have pointed out a major potential problem with standard estimations of the rate of growth or dissolution of calcite, and derived a new theory to explain those results. In the past year we tested how well the model predicted growth under variable saturation states and in the presence of growth inhibitors. Additionally, we have contributed to our understanding of biological influences of minerals and improved our ability to predict the rate of dissolution of iron (oxy)(hydr)oxides.

Contributions to Other Disciplines:

Our findings will have ramifications for the Materials Science and Crystal Growth disciplines, as well as environmental science and/or physical chemistry.

Contributions to Human Resource Development:

Activities from this project led directly to the training of a new environmental consultant. That is, pending completion of her degree, the Ph.D. student supported by this project is beginning a new position at the Newfields, Inc. environmental consulting firm.

Contributions to Resources for Research and Education:

The project funded two summer internships for Ms. Kari Salomon, an 8th grade Earth Science teacher. During these internships, she learned about biogeochemistry and created new lesson plans, exercises and laboratory experiments that she incorporated into her curriculum.

Contributions Beyond Science and Engineering:

This project has contributed to inspiring students with the wonder of the biological world, and helped a middle school teacher become up to date in her knowledge of the current state of geochemistry.

Conference Proceedings

Stack, AG, COLL 112-Computational prediction of kinetics of processes at mineral-water interfaces and aqueous ions, "APR 06-10, 2008", ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY, 235: - 112-COLL APR 6 2008

Wigginton, NS;Rosso, KM;Hochella, MF;Stack, AG, COLL 111-Long-range electron transfer between bacterial multiheme cytochromes and hematite (001) surfaces, "APR 06-10, 2008", ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY, 235: - 111-COLL APR 6 2008

Stack, AG;Zhang, MN;DiChristina, TJ, GEOC 17-Respiration on amorphous iron oxyhydroxides by Shewanella oneidensis: Attachment and dissolution morphology, "AUG 17-21, 2008", ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY, 236: - 17-GEOC AUG 17 2008

Stack, AG, Crystal growth and dissolution in terms of the rates of attachment of ions from solution and their detachment, "JUN 13-18, 2010", GEOCHIMICA ET COSMOCHIMICA ACTA, 74 (12): A987-A987 Suppl. 1 JUN 2010

Bracco, JN;Grantham, MC;Stack, AG, Calcite ($CaCO_3$) growth as a function of calcium-to-carbonate ratio in the presence of strontium, "JUN 13-18, 2010", GEOCHIMICA ET COSMOCHIMICA ACTA, 74 (12): A116-A116 Suppl. 1 JUN 2010

Categories for which nothing is reported:

Organizational Partners

Any Book

Any Web/Internet Site

Any Product

Research Activities

In performing the work funded by NSF proposal EAR 0643139 entitled, "Testing Molecular Mechanisms for Growth and Dissolution Reactions on Calcite Surfaces", we have spent the first year addressing the first hypothesis discussed in the proposal:

Hypothesis 1: Step movement on calcite surfaces observed by atomic force microscopy (AFM) can be fit by the same model for both growth and dissolution, where kink site formation and propagation are limiting.

The motivation behind testing this particular hypothesis is that it is commonly assumed that kink site concentrations and activation energy for kink site formation play a key role in determining the rate as well as the morphology of the surface in the calcite growth and dissolution literature (e.g., Teng et al., 2000; Jordan and Ramensee, 1998). Furthermore, the kink site concentration plays a fundamental role in the action of impurities such as magnesium (Davis et al., 2000) strontium (Astilleros et al., 2003) and manganese (Astilleros et al., 2002). While many measurements of step velocities exist, somewhat surprisingly, an estimate of kink site density has not been made, although some models implicitly rely on this (Liang et al., 1996; Liang and Baer, 1997; McCoy and LaFemina, 1997; Teng et al., 1999). We proposed to estimate this quantity using atomic force microscopy (AFM) by measuring step velocity as a function of supersaturation and temperature to infer the kink site density, formation and activation energies.

The model that will be used is that of Higgins et al., (2000), who indirectly measured the kink site concentration, formation and activation energies for barite growth using atomic force microscopy and fitting the results to a one-dimensional birth and spread model. Here, the step retreat rate, v (nm/s), is limited by both the rates of formation double-kink site formation within the step (R_{kk}, $nm^{-1}s^{-1}$) and single kink site propagation rate (R_k, nm/s; see Figure 1c): $v \cong a(2R_{kk}R_k)^{1/2}$, where a is the unit lattice dimension (nm). The step velocity is related to the bulk dissolution rate, R (mol/m^2s), by: $R \cong V_m h_m R_{pn}^{1/3}(v/a)^{2/3}$, where h_m is the height of a monolayer plane (nm) and R_{pn} is the pit nucleation rate. The rate of single kink site formation is described by: $R_k = bw_-(S-1)$ where S is the saturation state (IAP/K_{sp}), w_- is the detachment frequency at kinks and is, $w_- = w_0 exp(-E_a/RT)$ and E_a is the activation energy. The rate of double kink formation is described as $R_{kk} = (2w_-/a)*S(S-1)exp(-2\epsilon/kT)$ where ϵ is the double kink formation energy. Combining these expressions with the velocity expression above gives us the final equation: $v \cong 2bw_0*exp(-E_a/RT)*(S-1)*(S^{1/2})*exp(-2\epsilon/kT)$. The activation energy and the kink site formation energy can be estimated from a best fit of the measurements of the step velocity as a function of the supersaturation and temperature. One drawback of this model is that it makes no distinction between the formation and activation energies for double-kink formation energies and single-kink propagation. Since they have a different number of bonds to the surface, their rate of detachment should be different. Thus, these two reactions should be distinguished, but the formulation does not support a unique determination for an increased number of parameters.

Prior to measuring step velocities, our AFM needed to be adapted for better flow through and temperature control. To accomplish this, we designed a custom fluid cell that give a more direct flow path of fluid than either the stock cell on our Agilent PicoPlus microscope or the stock cell on a Veeco multimode system. Our initial flow cell was made out of acrylic, which we discovered leached contaminant into the crystal growth solution at high temperature. Thus, we created a new fluid cell out of polycarbonate with a much better chemical resistance at high temperature. This fluid cell is giving much more reliable data, in addition to containing a thermocouple port that allows us to monitor the reaction temperature in the cell directly. Secondly, we designed a jacketed flow system that keeps inlet solution lines at the desired

temperature prior to their entrance to the fluid cell. Using this system we have established an operational range of 5-70 °C, which should be more than enough to collect reasonable kinetic data on calcite.

Educational Activities and Broader Impacts

This research could have some far-reaching benefits beyond the geochemical community. Already, the PI has included the early findings from this early portion of the work in his invited talk at the "Physical Chemistry at Environmental Interfaces" symposium at the spring 2008 American Chemical Society meeting. Long term effects could have implications in industrial settings where crystal growth modification is desirable. Such applications include prevention of barite scale problems in the oil industry where an economic method to inhibit their growth would enhance the lifetime of well casings. The economic growth of large, high purity optics such as potassium dihydrogen phosphate is necessary for use in high powered lasers, e.g., the National Ignition Facility at Lawrence Livermore National Laboratory. It is desirable to discover growth modifiers that would allow the minimum sized crystal to be grown to allow a large optic to be cut from it (De Yoreo et al., 2002). Our understanding of crystal growth modification is rudimentary at best and attempts to design additives to accomplish this have met with little success (Thomas et al., 2004). Further areas of interest include the development of nano-devices such as micro-patterned single crystals and improved heterogeneous catalysis techniques that may yield exciting new technologies. The baseline understanding of mineral growth and dissolution and how it is controlled in biological systems could be useful in these settings.

There are educational activities resulting from the proposal as well. Data from the research is already being used to illustrate mineral growth and dissolution processes to students in the PI's "Water Quality Modeling" course. Presently, a graduate student has not been found to perform the work, but one is hoped to be arriving at Georgia Tech this fall. The salary money is being used to pay Ms. Meg Grantham, a laboratory technician with experience in crystal growth. Additionally, Ms. Kari Salomon, a middle school teacher from the metro Atlanta area will be doing an internship this summer in the laboratory of the PI. This is through the framework established through the Georgia Inter-Fellowships for Teachers through the Center for Integrating Science Mathematics and Computing center (CEISMC) at Georgia Tech. The internship will will be six weeks starting in July. This is possible because the methods for measurement of the step velocities has been developed already so the measurements themselves as well as the interpretation of the results are relatively routine. To evaluate the success of the work, the teacher prepares a brief presentation of her findings to be reported to the CEISMC at the end of the internship and includes some lesson plans that incorporate her experiences in the laboratory into her curriculum.

References

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Major Findings

We are in the process of making step velocity measurements as a function of saturation and temperature. Step velocities are being measured in the method of Teng (2000), that is, using a combination of single-point measurements within an image as well as continuous monitoring the position of a step as a function of time at a single location with the slow-scan axis disabled. Contrary to the more complex model discussed in the Research Activities statement that we will apply, we have first been fitting the step velocity measurements using a simple Arrhenius relationship. This has been done in order to compare with existing step velocity measurements as a function of temperature made by Wasylenki et al. (2005) who measured calcite growth in the presence of the known growth modification agent, Mg^{2+} (De Yoreo and Dove, 2004), and at an ionic strength of 0.1 M, also known to have an effect on growth and dissolution processes (Dove and Elston, 1992). As shown in Figure 1a, step velocity measurements are made as a function of dissolved ion concentration at a given temperature (no added electrolyte). This was done for three different temperatures thus far, 5, 25 and 50 °C. The step velocity, v (nm/s), is described as: $v = \omega\beta(IAP)$ where ω is the molecular volume of calcite, β is the kinetic coefficient and IAP is the ion activity product. Figure 1b shows the Arrhenius plot for how the kinetic coefficient changes with temperature. The slope of this plot gives the activation energy, E_a. The activation energy measured in Figure 1b is +23 kJ/mol, substantially smaller than in the presence of higher ionic strength and Mg^{2+}. The data need to be verified however, because the fluid cell used was the acrylic one, which could have been leaching material into the fluid cell, especially at high temperature.

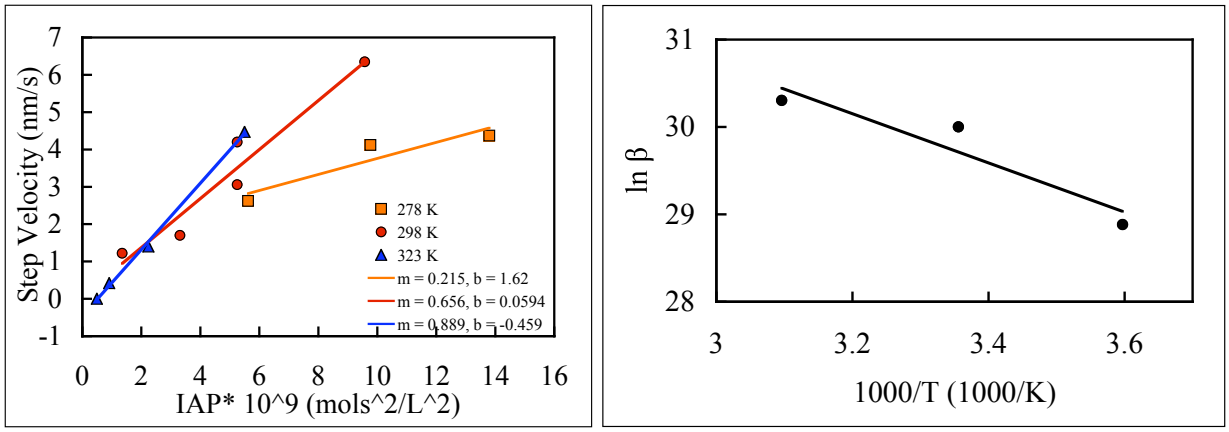

Figure 1a (left) and 1b (right). Step velocity measurements of calcite growth. Figure 1a shows the step velocity as a function of the ion activity product (IAP). The slope at each temperature is measured and the kinetic coefficient (β) is estimated. An Arrhenius plot is made (Figure 1b) that plots the natural log of the kinetic coefficient as a function of 1000/T. The slope of this plot yields the activation energy, E_a = +23 kJ/mol. The data point at 50 °C (the furthest to the left in Figure 1b) is being verified with a new fluid cell as there is some reason to believe that experiment was contaminated.

References

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